

University of Groningen

Synthesis and complexation characteristics of phenanthroline and bipyridine diols

Koning, B.; Boer, J.W. de; Meetsma, A.; Kellogg, R.M.

Published in:
 Arkivoc

DOI:
[10.3998/ark.5550190.0005.213](https://doi.org/10.3998/ark.5550190.0005.213)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
 Publisher's PDF, also known as Version of record

Publication date:
 2004

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Koning, B., Boer, J. W. D., Meetsma, A., & Kellogg, R. M. (2004). Synthesis and complexation characteristics of phenanthroline and bipyridine diols. *Arkivoc*, 2004(2), 189-205.
<https://doi.org/10.3998/ark.5550190.0005.213>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Synthesis and complexation characteristics of phenanthroline and bipyridine diols

B. Koning,^a J.W. de Boer,^b A. Meetsma,^b and R.M. Kellogg^a

^a *Syncom BV, Kadijk 3, 9747 AT Groningen, The Netherlands*

^b *Organic and Molecular Inorganic Chemistry, Stratingh Institute, Department of Chemistry
University of Groningen, Nijenborgh 4, Groningen 9747 AG, The Netherlands*

E-mail: R.M.Kellogg@syncom.nl

Dedicated to Professor Binne Zwanenburg on his 70th Anniversary

Abstract

Neocuproine (2,9-dimethyl-1,10-phenanthroline) **1** was converted to achiral and chiral tetradentate phenanthroline diols **3a-c** by addition to benzophenone, adamantanone and camphor, respectively. Analogously 6,6'-dimethyl-2,2'-bipyridine **2** was converted to diol **7a** on base-induced addition to benzophenone. Reactions with benzophenone and adamantanone proceeded smoothly although small amounts of mono adducts were also formed. Functionalization of **1** with (*R*)-camphor failed under the standard conditions. However, conversion of the lithio derivative **5** to the cerium chloride derivative **6** and subsequent reaction with (*R*)-camphor led to the phenanthroline diol **3c**. Complexes of the diols **3** and **7** with zinc and copper were prepared. X-ray analysis of the zinc complex **20** of diol **7a** revealed a five coordinate zinc ion that is firmly embedded in the ligand. X-ray analysis of the Cu(acac)₂ complex **21** of diol **7a** unexpectedly revealed this to be an acetate bridged di-copper species. This copper complex forms on recrystallization from ethyl acetate. The initial acac-complex apparently hydrolyses the ethyl acetate to provide the bridging acetate found in the di-copper complex **21**. From 4,7-dichloro-2,9-dimethyl-1,10-phenanthroline **13** a "doubly armed" derivative **18** was prepared by substitution with two tetraethylene glycol "arms" followed by suitable derivatisation. A bridged derivative **19** was prepared by ring closure with an amine of the ditosylated tetraethylene glycol derivative. Attempts to prepare copper complexes of **18** and **19** were inconclusive.

Keywords: phenanthroline, bipyridine, neocuproine, zinc and copper complexes, benzophenone, adamantanone, camphor, diols, ligands, di-copper bridges, doubly armed ligands.

Introduction

Both 1,10-phenanthroline and 2,2'-bipyridine are attractive building blocks that are often incorporated, usually as their metal complexes, into various host molecules. In addition the metal complexes of these two molecules are frequently employed for catalytic reactions. The two

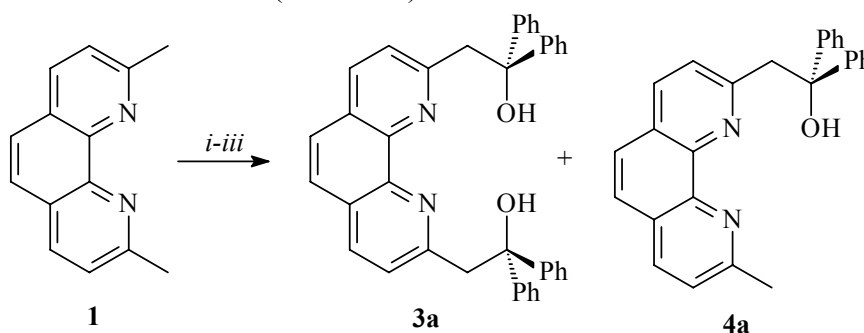
nitrogen atoms in each molecule are ideally placed for cooperative binding of many metal cations.¹ For example metal ion complexes with functionalised 1,10-phenanthrolines have been used as catalyst for the enantioselective hydrolysis of *N*-protected amino acid esters,² for the oxidative cleavage of DNA,³ in palladium catalysed allylic substitutions⁴ and in enantioselective reduction of acetophenone.^{5,6} Metal complexes of 2,2'-bipyridines have also been widely used.⁷ Functionalised 2,2'-bipyridines have been employed in the enantioselective alkylation of aldehydes,^{8,9} in the enantioselective hydrosilylation of ketones,¹⁰ in asymmetric allylation reactions,¹¹ in cyclopropanation of styrene,¹² in palladium catalysed allylic substitutions,¹³ and as herbicides.¹⁴ These building blocks have been used for, for example, the synthesis of (mixed) crown ethers,¹⁵ catenates and catenands,¹⁶ and for the formation of macromolecular structures and grids.¹⁷

In analogy to methodology that we have developed for the functionalisation of 2,6-dimethylpyridines to prepare tetradentate ligands¹⁸ we have now prepared similar derivatives of 2,9-dimethyl-1,10-phenanthroline ("neocuproine", **1**) and the analogous 6,6'-dimethyl derivative **2** of 2,2'-bipyridine.

Results and Discussion

Synthesis

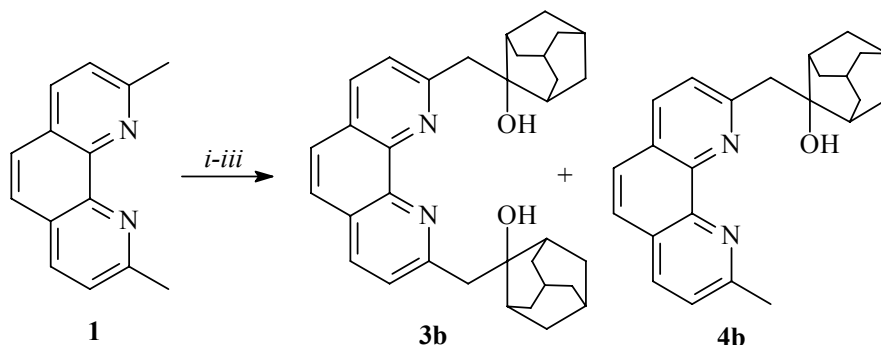
When **1** was deprotonated at the methyl groups with 2.5 equiv. of LDA at -80°C and subsequently quenched with benzophenone phenanthroline diol **3a** was obtained in 55% yield together with 15% of material judged to be the mono-adduct **4a** on the basis of the $^1\text{H-NMR}$ spectrum of the crude reaction mixture (Scheme 1).



Scheme 1. Reagents and conditions: *i*, LDA, -80°C ; *ii* benzophenone; *iii* 2M NH_4Cl .

The bis-adduct **3a** was separated from the mono-adduct by washing with hot ethanol and was purified by recrystallization from chloroform/acetonitrile/hexane. Use of a smaller excess of LDA led to an increase in formation of the mono-adduct. Attempts to deprotonate **1** with *n*-butyllithium gave rise to undefined side products that probably result from addition of an *n*-butyl group to the ring system.

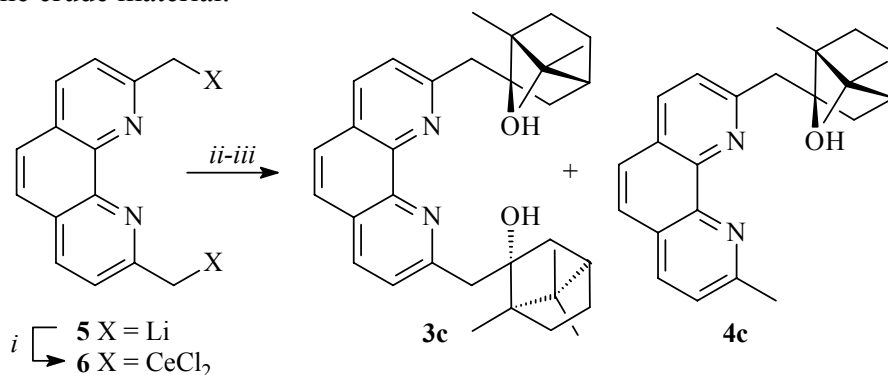
When adamantanone instead of benzophenone was used for the functionalization of **1** the bis-adduct **3b** was obtained on recrystallisation from ethyl acetate in 49% yield (Scheme 2). The mono-adduct **4b** was isolated but was not characterized further.



Scheme 2. Reagents and conditions: *i*, LDA, -80°C ; *ii* adamantanone; *iii* 2M NH_4Cl .

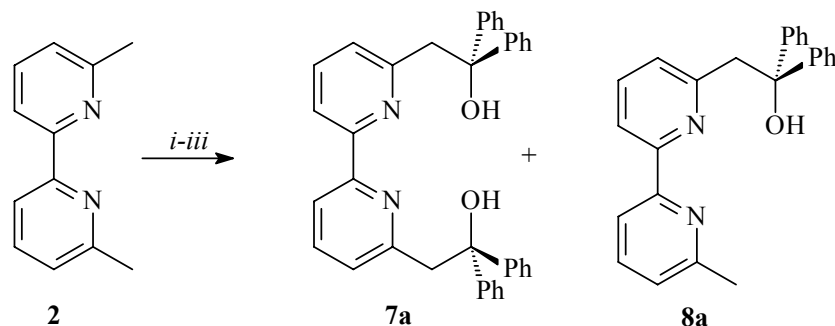
The lower yield of **3b** related to the benzophenone adduct is probably due to the lower reactivity of the carbonyl functionality of adamantanone compared to that of benzophenone.

When (*R*)-camphor, which is even less reactive than adamantanone and which easily undergoes enolization, was allowed to react with the bislithiated **5** derived from **1** formation of neither the desired diol **3c** nor the mono-adduct **4c** was observed. At -80°C no reaction at all occurs. However, when the temperature was raised to -50°C decolorization occurred indicating the disappearance of the dilithio adduct. Workup afforded only starting material indicating that at -50°C (*R*)-camphor enolises rather than undergoing attack at the carbonyl functionality. In order to effect addition to (*R*)-camphor the more oxaphilic and less basic cerium derivative was generated by exchange with lithium.¹⁹ The dilithio derivative **5** derived from **1** was converted to the CeCl_2 species **6** by addition of $\text{CeCl}_3 \cdot \text{THF}$ after lithiation. When **6** was stirred with $\text{CeCl}_3 \cdot \text{THF}$ for 1 hour at -78°C and quenched with (*R*)-camphor the chiral phenanthroline diol **3c** was formed in 65% yield (Scheme 3). Concentration of the mother liquor gave a small amount of the presumed mono-adduct **4c**, which was characterized only on the basis of the $^1\text{H-NMR}$ spectrum of the crude material.



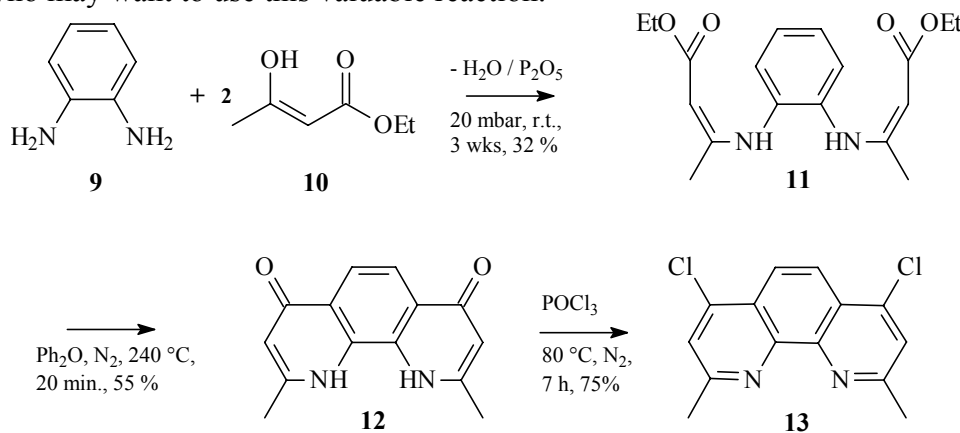
Scheme 3. Reagents and conditions: *i*, $\text{CeCl}_3 \cdot \text{THF}$, -80°C ; *ii* (*R*)-camphor; *iii* 2M NH_4Cl .

Functionalization of 6,6'-dimethyl-2,2'-bipyridine **2** was carried analogously to the procedure described for **1**. Lithiation of **2** with 2.5 equiv. of LDA and subsequent addition of benzophenone afforded the bipyridine diol **7a** in 49% yield along with 29% of the mono-adduct **8a**, which was characterized fully (Scheme 4). The mono and bis-adducts could be separated by making use of the lower solubility of the bis-adduct in methanol.



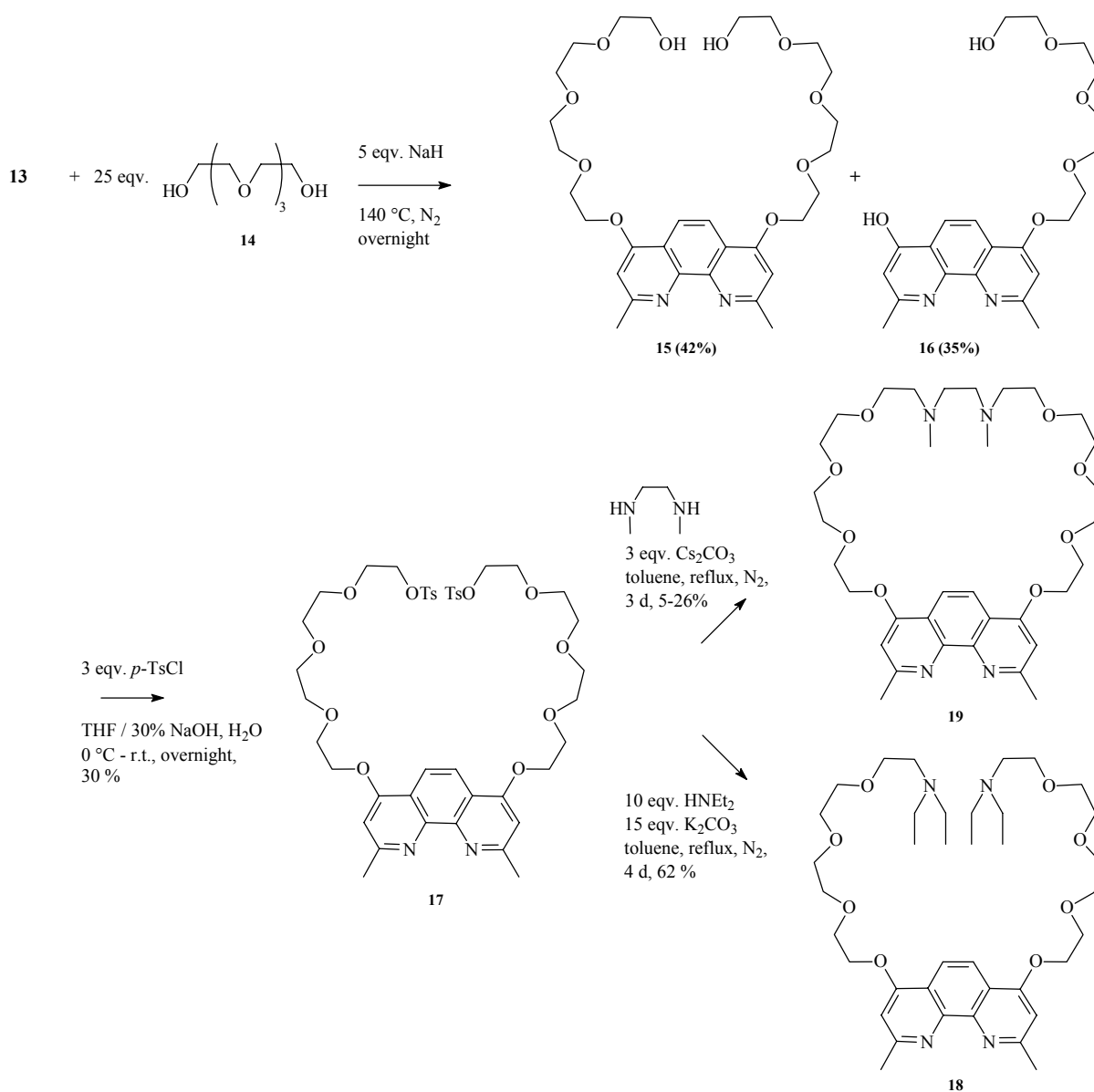
Scheme 4. Reagents and conditions: *i*, LDA, -80°C; *ii* benzophenone; *iii* 2M NH₄Cl.

We have also briefly examined the possibilities of incorporation of extra complexation possibilities not through the methyl groups but through macrocyclic rings that bridge the diaza coordination system. These investigations have been confined to the phenanthroline nucleus. The starting point was 4,7-dichloro-2,9-dimethylphenanthroline **13** prepared by the method of Schmitt et al.²⁰ as shown in Scheme 5. We made numerous attempts to speed up or to increase the scale (in our hands maximally 0.1 mol) of this extremely useful reaction but with limited success. The conversion of **10** to **11** is very slow but works well, and can be carried out on reasonable (20-30 g) scale. The bottleneck is the conversion of **12** to **13**. Schmitt et al describe this conversion in quantitative yield on 1 g scale. In our hands increase of scale to 2-3 g led to yields of **13** between 63-95%. The greatest problem is the work-up procedure for the isolation of **13**. The hot reaction mixture is poured into an ice:water mixture and the water layer is subsequently brought to pH 14 with conc. NaOH, which has to be added *very slowly* ensuring that the reaction temperature does not exceed 45-50°C. We mention these details for the benefit of others who may want to use this valuable reaction.



Scheme 5. Synthesis of 4,7-dichloro-2,9-dimethylphenanthroline

Two derivatives have been prepared, one with two arms and the other bridged. The syntheses of the “armed” derivative **18** and the “closed” derivative **19** are shown in Scheme 6.



Scheme 6. Synthesis of phenanthroline derivatives.

The doubly armed tosylate **17** is the key intermediate for preparation of both compounds. Ring closure to **19** proceeded in 7-26% yield. Both end products were characterized by NMR spectroscopy and ES-MS. It was not possible to obtain exact mass spectra for either **18** or **19**.

Complexations with metals

Ligands with a phenanthroline or bipyridine moiety are usually strong metal chelating agents. The phenanthroline and bipyridine based tetradentate diols were also expected to form stable

complexes with zinc and copper. Of particular interest was whether the hydroxy groups would also participate in coordination. When zinc perchlorate heptahydrate was added to a suspension of phenanthroline diol **3c** in a mixture of $\text{CD}_3\text{CN}/\text{CDCl}_3$ (9:1) a complex was formed as deduced from ^1H NMR spectroscopy. A downfield shift of 0.5 ppm for the aromatic protons (referred to the free ligand in the same solvent mixture) was observed indicating complexation of the phenanthroline moiety. The benzylic protons gave a set of 4 signals, which indicates that these protons are diastereotopic and that the complex has a locked conformation on the NMR scale. This observation is consistent with coordination of the hydroxy groups. Furthermore a signal for the hydroxy groups was observed at δ 5.40, which suggests strongly that the hydroxy groups, despite coordination, are not deprotonated. Although a crystalline complex with a correct elemental analysis (no water) was isolated, attempts to determine the structure by X-ray methods were unsuccessful.

After addition of zinc perchlorate heptahydrate to a suspension of the bipyridyl diol **7a** in a mixture of CD_3CN and CDCl_3 (9/1) the material slowly dissolved and a complex **20** was formed. Again complexation gave rise to a downfield shift of the pyridine protons, though to a smaller extent than observed for the phenanthroline system **3c**. Furthermore the benzylic protons are shifted 0.4 ppm downfield (referred to the free ligand). The benzylic protons in this complex appear as a singlet, which could indicate some flexibility in the complex as a consequence of the possibility of torsion about the bipyridine bond. Also a signal for the hydroxy groups is observed at δ 7.48, indicative of the fact that deprotonation did not take place. More structural information for **20** was obtained from the X-ray structure.²¹ Crystals for X-ray were grown from ethyl acetate/acetonitrile and isothermal distillation of hexane into the solution.

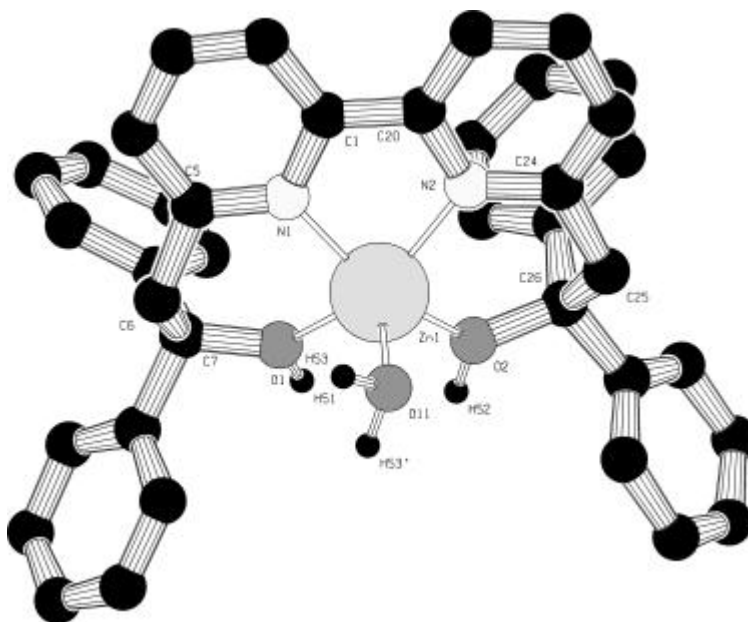


Figure 1: X-ray structure of **20** without the perchlorate counter ions.

Although an X-ray structure determination was severely hindered by persistent weakly scattering crystals and also broad reflections, ultimately a data set was gathered from which a successful structure determination was obtained (Figure 1). The crystal structure reveals a pentacoordinated zinc atom in a square pyramidal surrounding. The two hydroxy groups, the two nitrogen groups and an additional water molecule are involved in the binding of the zinc in a square pyrimidal fashion. The zinc is situated in the middle of the molecule, which roughly has a symmetry axis through the zinc, the water molecule and the bipyridine bond. The bipyridine bridge moiety is almost flat and the hydroxy groups are directed towards the zinc ion.

Complexes with copper were also easily formed. Addition of Cu(I)triflate.benzene complex to 2,2'-bipyridyl diol **7a** in acetonitrile under argon immediately afforded a red solution that turned blue after a few seconds of stirring indicating that the Cu(I) is converted to more stable Cu(II). This conclusion is also supported by the observation of a paramagnetic nucleus (by NMR) in solution. Since elemental Cu is not observed it is most probable that the Cu(I) is oxidized by the ligand. Complexation of Cu(acac)₂ with 2,2'-bipyridine diol **7a** in acetonitrile was more successful and a blue crystalline precipitate was formed. The ¹H NMR of this complex in chloroform revealed the presence of a paramagnetic nucleus and complexation with the ligand. Whether or not the alcohol functionalities are deprotonated is unclear from the ¹H NMR spectra. Suitable crystals for X-ray diffraction were grown by recrystallization from hot ethyl acetate. Surprisingly X-ray analysis showed a di-copper complex **21** in which the copper ions are bridged by acetate groups and the hydroxylates.²¹ The asymmetric unit of the crystals consisted of two di-Cu complexes and four heavily disordered acetate molecules (Figure 2).

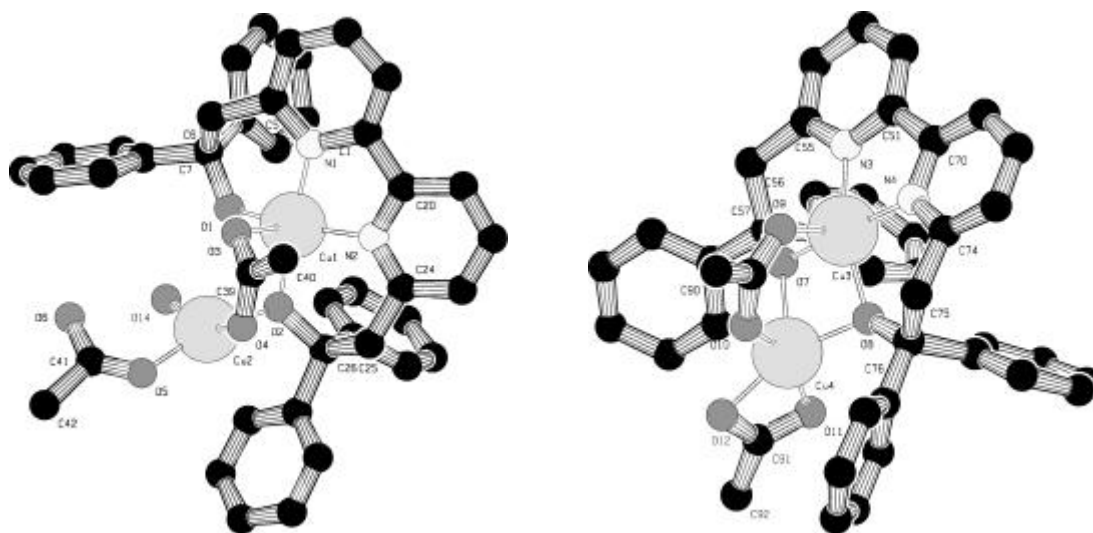


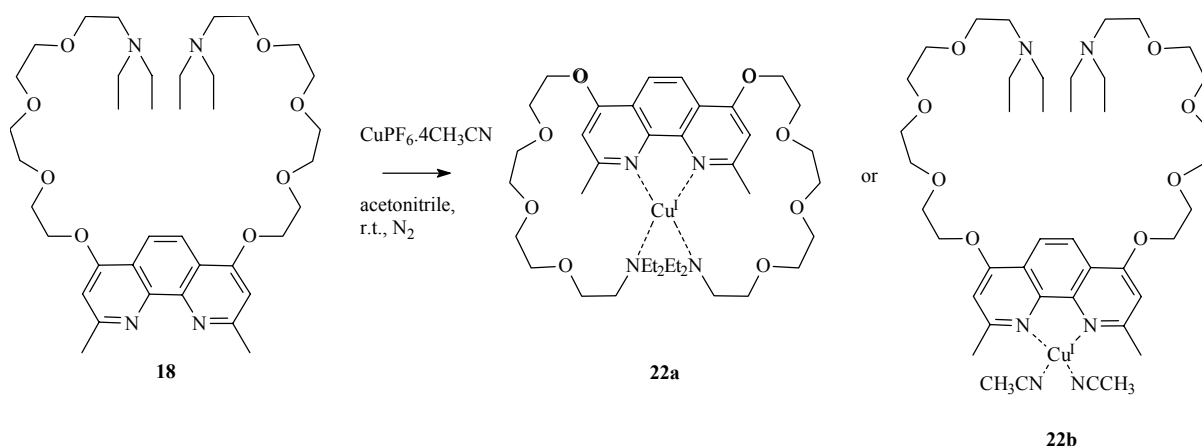
Figure 2: X-ray structure of residues 1(left) and 2 of complex **21**.

In the first residue (left) one copper ion is symmetrically bond to the bipyridine nitrogens, an acetate oxygen and the hydroxylates of the ligand to form square pyramidal surroundings (Cu(1)...N(1) 1.954 Å; Cu(1)...N(2) 2.000 Å; Cu(1)...O(3) 2.342 Å; Cu(1)...O(1) 1.913 Å;

Cu(1)...O(2) 1.913 Å). The second copper ion also coordinates to one of the hydroxylates and is bridged to the other copper ions through the acetate molecule. A second acetate molecule is coordinated to this copper. The fourth coordination site of this copper is occupied by a water molecule. The distance between the two copper ions Cu(1) and Cu(2) is 3.151 Å, which is comparable to the distances found for other di-copper complexes.²² The ligand backbone is slightly twisted; a torsion angle of -5.1° is observed. The second residue (right) embeds, analogously to the first residue, two copper ions. These ions are bridged by both hydroxylates and by an acetate molecule. The distance between the two copper ions in this structure is somewhat shorter (Cu(3)...Cu(4) 2.8861 Å). The first copper ion is embedded in the ligand and is square pyramidal coordinated. The second copper ion coordinates to both hydroxylate groups (Cu(3)...O(7) 2.225 Å; Cu(3)...O(8) 1.932 Å). No coordination of water is found in this residue. The bipyridine backbone is nearly flat, a torsion angle of -4.2° being observed.

Although the synthesis of this complex began with free ligand and Cu(acac)₂ the inclusion of the acetate molecules in the X-ray structure can be explained by the hydrolysis of ethyl acetate upon heating. Probably water present in the complex gives rise to the hydrolysis.

Attempts to form copper complexes with bridged phenanthroline **19** using either Cu⁺¹ or Cu⁺² salts were inconclusive. Marginally more success was obtained with the "armed" derivative **18**. Attempts to form complexes with CuCl₂ led to complex mixtures, which, on the basis of ES-MS appeared to consist of Cu⁺ complexes. We were surprised to observe reduction. In view of these observations we examined complexation of **18** by the copper(I) salt CuPF₆. In principle two types of complex, **22a** or **22b**, might be formed as indicated in Scheme 7.



Scheme 7. Complexation of Cu(I).

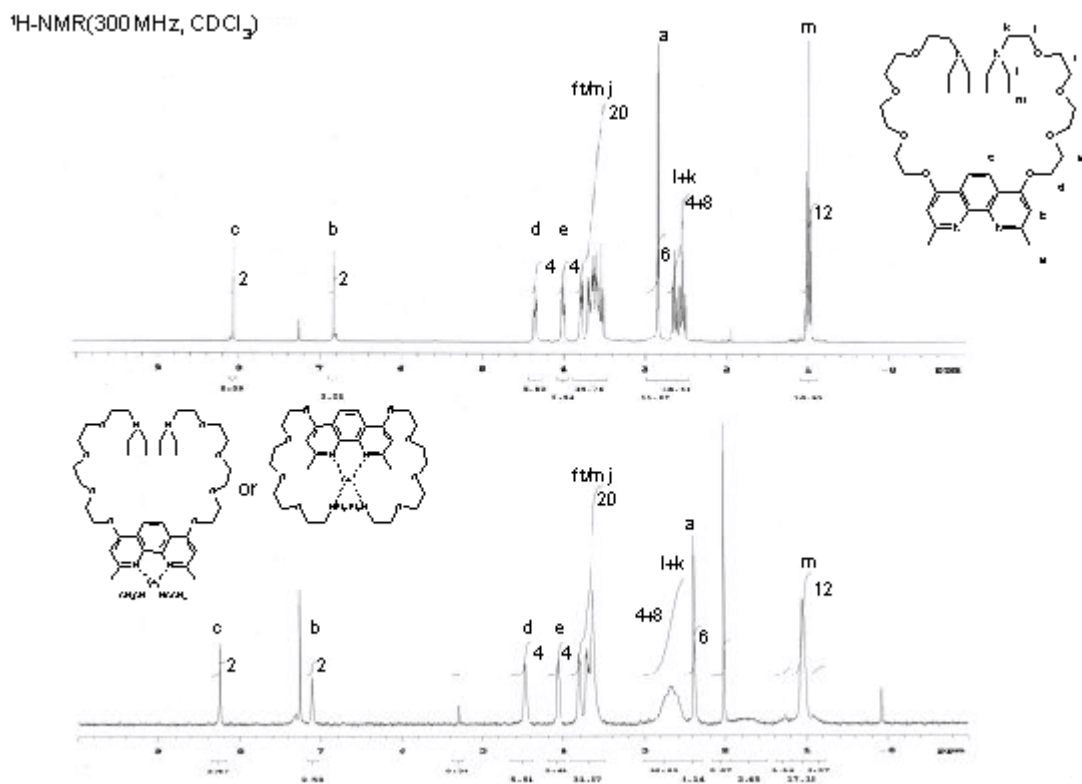


Figure 3: 300 MHz ¹H-NMR spectra of free ligand 18 (top) and of the Cu(I) complex of this ligand (bottom) in CDCl₃.

The ¹H-NMR spectrum (Fig. 3) is consistent with complexation between the Cu⁺ and the ligand. Protons H_b and H_c show a downfield shift of δ 0.27 and δ 0.17 ppm, respectively, relative to the free ligand. The protons H_a of the methyl group showed a large upfield shift from δ 2.84 to δ 2.38 ppm. The signals of the protons of the methylene group adjacent to the nitrogens of the arms (H_k and H_l) showed extensive line broadening, although the signals for these protons did not show a large shift. The signals of the other protons showed also some line broadening, but little up or downfield shifts.

Based on the observed shifts of the protons from the phenanthroline moiety it can be concluded that the Cu⁺ cation is bound to the ligand via its phenanthroline nitrogens. Whether the third and fourth coordination sites of the Cu⁺ are occupied by the nitrogens of the arms of the ligand, by two solvent molecules or by another ligand is not clear.

Conclusions

Phenanthroline diols **3** and bipyridine diols **7** have been prepared using the methodology described previously for the synthesis of pyridine diols.¹⁸ Monoadducts **4** and **8**, respectively, were formed as a side products but can easily be removed. Although the nucleophilicity of the

dilithiated **1** and **2** is most likely less than that of lithiated 2,6-lutidine, reactions with benzophenone and adamantanone occur smoothly. Reaction with (*R*)-camphor, however, was thwarted by the lower nucleophilicity and the possibility of the ketone to enolise. These problems can be neatly solved by conversion to the cerium derivative.

It is clear that the hydroxyl groups of these ligands also readily participate in coordination to metal ions.

Experimental Section

General Remarks: All reactions were carried out under an Ar atmosphere. The following solvents were distilled prior to use: THF, diethyl ether and toluene were distilled from Na wire, acetonitrile was distilled over CaH₂, and dichloromethane, ethyl acetate, and hexane were distilled over P₂O₅. Column chromatography was performed on alumina (Merck 90, II/III, 0.063-0.200 mm) or silica gel (Aldrich 60, 230-400 mesh). Elemental microanalyses were carried out in the analytical department of the University of Groningen. X-ray diffraction studies were carried out in the Crystal Structure Center of the university. ¹H and ¹³C spectra were recorded using a Varian Unity Plus Varian 500, a Varian VXR 300 instrument or a Genuine 200 Instrument. The chemical shifts are expressed relative to TMSCl for ¹H NMR and to CDCl₃ for ¹³C NMR. *NOESY*²³, and *COSY*²⁴ spectra were performed using standard Varian pulse programs. Deuterated solvents were dried over an Al₂O₃ (activity 1) column just prior to use. Melting points (uncorrected) were determined on a Mettler FP-2 melting point apparatus, equipped with a Mettler FP-21 microscope. Reagents and starting materials used were obtained from Aldrich, Fluka or Acros Chimica and used as received, unless noted otherwise. Anhydrous neocuproine was obtained by recrystallization from benzene. CeCl₃·7H₂O was dried according to the literature.²⁵

2-[9-(2-hydroxy-2,2-diphenylethyl)-1,10-phenanthrolin-2-yl]-1,1-diphenyl-1-ethanol **3a**.

To a stirred solution of neocuproine **1**²⁶ (0.25 g, 1.2 mmol) in 50 mL of THF at -80°C was added LDA (2.0 M solution in THF/*n*-heptane, 1.5 mL, 3.0 mmol). After stirring for 1 h a solution of benzophenone (0.54 g, 3.0 mmol) in 5 mL of THF was added. Stirring was continued overnight and the reaction mixture was allowed to reach room temperature. The solution was quenched with 2M NH₄Cl and chloroform/acetonitrile (1:1) 100 mL was added. The solution was sonicated for 1 h and the layers were separated. The aqueous layer was washed with chloroform twice. The combined organic layers were dried over Na₂SO₄. After evaporation of the solvent the solid was washed with hot ethanol to yield the bis-adduct, which was crystallized from chloroform/acetonitrile/hexane to afford the bis-adduct **3a** as a hydrate (0.47 g, 0.8 mmol, 55%): mp 208-209 °C; ¹H NMR (300 MHz, CD₃CN): δ 1.53 (br, H₂O), 4.00 (s, 4H), 7.07 (m, 4H), 7.19 (m, 10H), 7.29 (d, *J* = 8.05 Hz, 2H), 7.57 (m, 8H), 7.95 (d, *J* = 8.05 Hz, 2H). δ; HRMS calcd

572.246; no proper HRMS could be obtained, $\text{Cl}(\text{NH}_3)$ gave a molecular ion at m/e 573. Anal. Calcd for $\text{C}_{80}\text{H}_{66}\text{N}_4\text{O}_5$: C, 82.59; H, 5.72; N, 4.82. Found C, 82.94; H, 5.84; N, 4.81.

2-({9-[(2-hydroxy-2-adamantyl)methyl]-1,10-phenanthroline-2-yl}methyl)-2-adamantanol **3b.**

A solution of neocuproine **1** (0.30 g, 1.44 mmol) in 50 mL of THF was cooled to -80°C and LDA (2.0 M solution in THF/*n*-heptane, 1.8 mL, 3.6 mmol) was slowly added. After stirring for 1 h adamantanone (0.54 g, 3.6 mmol) in 5 mL of THF was added. The mixture was quenched with 2M NH_4Cl and extracted with dichloromethane twice. The combined organic layers were washed with brine and dried over Na_2SO_4 . The bis-adduct **3b** was recrystallized from ethyl acetate to afford colorless needles (0.36 g, 0.71 mmol, 49%): mp $221\text{--}223^\circ\text{C}$; ^1H NMR (300 MHz, CDCl_3): δ 1.42 (m, 4H), 1.71 (m, 10H), 1.78 (m, 4H), 1.90 (m, 2H), 2.01 (m, 4H), 2.43 (m, 4H), 3.48 (s, 4H), 7.50 (d, $J = 8.3$ Hz, 2H), 7.73 (s, 2H), 8.16 (d, $J = 8.3$ Hz, 1H). ^{13}C NMR: δ 27.42 (d), 27.50 (d), 32.75 (t), 34.72 (t), 37.28 (d), 38.51 (t), 44.56 (t), 75.42 (s), 124.56 (d), 125.50 (d), 126.94 (s), 136.27 (d), 160.40 (s); HRMS calcd 508.309; found 508.309. Anal. Calcd for $\text{C}_{34}\text{H}_{40}\text{N}_2\text{O}_2$: C, 80.28; H, 7.93; N, 5.51. Found C, 80.28; H, 7.77; N 5.46.

(1*R*,2*S*)-2-[(9-[(1*R*,2*S*)-2-hydroxy-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]methyl)-[1,10]phenanthroline-2-yl)methyl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol **3c.**

A solution of CeCl_3 ²⁵ (1.61 g, 6.5 mmol) in 150 mL of THF was sonicated overnight and cooled to -80°C . Subsequently a previously prepared solution of lithiated neocuproine **5** (0.03N solution in THF, 1.6 mmol, 53 mL) was slowly added. The solution was stirred remained at -80°C for 1 h after which time (*R*)-camphor (0.87 g, 5.7 mmol) in 5 mL of THF was added. Stirring was continued for 3 h allowing the mixture to reach -10°C . Subsequently the mixture was quenched with 2M NH_4Cl and extracted with dichloromethane twice. The combined organic layers were washed with brine and dried over Na_2SO_4 . After removal of the solvent under reduced pressure the product was flushed over a short column (silica, ethyl acetate/hexane (1:3)). The obtained solid **3c** was recrystallized from ethyl acetate (0.53 g, 1.0 mmol, 65%): mp $199\text{--}201^\circ\text{C}$; ^1H NMR (300 MHz, CDCl_3): δ 0.51 (s, 6H), 0.77 (s, 6H), 1.09 (m, 2H), 1.17 (s, 6H), 1.42 (m, 6H), 1.66 (m, 4H), 2.35 (m, 2H), 3.28 (m, 4H), 6.6 (br, 2OH), 7.45 (d, $J = 8.05$ Hz, 2H), 7.67 (s, 2H), 8.11 (d, $J = 8.05$ Hz, 2H); ^{13}C NMR: δ 11.21 (q), 21.05 (q), 21.58 (q), 27.21 (t), 30.92 (t), 45.13 (d), 45.84 (t), 47.28 (t), 49.40 (s), 52.46 (s), 81.05 (s), 124.46 (d), 125.54 (d), 126.95 (s), 129.12 (s), 136.35 (d), 161.31 (s); HRMS calcd 512.340; found 512.340. Anal. Calcd for $\text{C}_{34}\text{H}_{44}\text{N}_2\text{O}_2$: C, 79.65; H, 8.65; N, 5.46. Found C, 79.24; H, 8.79; N, 5.44.

2-[3'-(2-hydroxy-2,2-diphenylethyl)[2,2'-bipyridyl]-6-yl]-1,1-diphenyl-1-ethanol **7a.**

The 2,2'-bipyridyl **2**²⁷ (0.16 g, 0.87 mmol) was dissolved in 25 mL of THF and lithiated at -80°C with LDA (2.0 M solution in THF/*n*-heptane, 1.1 mL, 2.2 mmol). After stirring for 1 h at -80°C a solution of benzophenone (0.40 g, 2.2 mmol) in 5 mL of THF was added. The mixture was allowed to reach ambient temperature in 3 h and was quenched with 2M NH_4Cl . The mixture

was extracted with dichloromethane twice and the combined organic layers were washed with brine and dried over Na_2SO_4 . After removal of the solvent the solid was washed with methanol and recrystallized from chloroform/hexane to afford the bis-adduct **7a** as hydrate (0.23 g, 0.43 mmol, 49 %): mp > 230 °C; ^1H NMR (300 MHz, CDCl_3): δ 1.56 (br, H_2O), 3.78 (s, 4H), 7.04 (m, 2H), 7.11 (m, 4H), 7.20 (m, 8H), 7.40 (m, 8H), 7.52 (br, 2OH), 7.60 (t, $J = 7.69$ Hz, 2H), 7.86 (d, $J = 8.06$ Hz, 2H). ^1H NMR (300 MHz, $\text{CD}_3\text{CN}/\text{CDCl}_3$): δ 3.53 (s, 4H), 6.82 (m, 4H), 6.94 (m, 8H), 7.00 (d, $J = 7.32$ Hz, 2H), 7.22 (m, 8H), 7.50 (m, 4H); ^{13}C NMR: δ 46.92 (t), 78.32 (s), 118.91 (d), 124.91 (d), 128.98 (d), 126.48 (d), 127.90 (d), 138.07 (d), 146.94 (s), 153.77 (s), 158.57 (s); HRMS calcd 548.246; found 548.246 Anal. Calcd for $\text{C}_{38}\text{H}_{34}\text{N}_2\text{O}_3$: C, 80.54; H, 6.05; N, 4.94. Found C, 80.85; H, 5.83; N 4.99.

The methanolic solution was concentrated and the solid was recrystallized from ethanol to afford the mono-adduct **8a** as a white solid, (0.09 g, 0.25 mmol, 29%): mp 194-195 °C; ^1H NMR (300 MHz, CDCl_3): δ 2.55 (s, 3H), 3.74 (s, 2H), 7.00 (d, $J = 7.7$ Hz, 1H), 7.11 (m, 3H), 7.19 (m, 4H), 7.43 (m, 4H), 7.62 (m, 2H), 7.87 (br, OH), 7.93 (d, $J = 8.1$ Hz, 1H), 8.14 (d, $J = 7.5$ Hz, 1H); ^{13}C NMR: δ 24.52 (q), 46.87 (t), 78.35 (s), 117.85 (d), 119.07 (d), 123.39 (d), 124.49 (d), 126.03 (d), 126.40 (d), 127.87 (d), 137.18 (d), 137.81 (d), 147.05 (s), 154.90 (s), 157.92 (s), 158.31 (s); HRMS calcd 366.173; found 366.173 Anal. Calcd for $\text{C}_{25}\text{H}_{22}\text{N}_2\text{O}$: C, 81.94; H, 6.05; N, 7.64. Found C, 81.44; H, 6.07; N, 7.46.

2-[2-(2-{2-[7-(2-{2-[2-(2-hydroxy-ethoxy)-ethoxy]-ethoxy}-ethoxy)-ethoxy]-ethanol (16) and 7-(2-{2-[2-(2-hydroxy-ethoxy)-ethoxy]-ethoxy}-ethoxy)-ethoxy)-2,9-dimethyl-[1,10]phenanthrolin-4-ol (15)

1.18 g (29.5 mmol NaH) sodium hydride (60% dispersion in oil) was washed twice with 10 ml of hexanes and was then added carefully to 26.3 g (135 mmol) tetraethyleneglycol **14**. The mixture was stirred for one hour at room temperature. 1.50 g (5.41 mmol) 4,7-dichloro-2,9-dimethyl-1,10-phenanthroline **13** was added and the resulting mixture was stirred at 140 °C for 18 hours. The reaction mixture was allowed to cool to room temperature and was subsequently poured onto 150 ml of ice-water and 50 ml of CH_2Cl_2 was added. The organic layer was separated and the water layer was extracted three times with 50 ml of CH_2Cl_2 . The combined organic layers were washed once with 50 ml of brine. After drying on Na_2SO_4 , the solvents were evaporated *in vacuo*. The di- and mono-substituted products (**15** and **16**) could be isolated by two successive flash column chromatographic separations (silica; $\text{CHCl}_3/\text{MeOH}$ 9:1) yielding **15** (1.40 g, 2.36 mmol, 43 %) as a viscous, colorless oil and **16** (35 %) as a colorless solid respectively. **15** ^1H -NMR (CDCl_3 , 300 MHz): δ 2.49 (br s, 2H), 2.86 (s, 6H), 3.56-3.59 (m, 4H), 3.63-3.72 (m, 16H), 3.79-3.83 (m, 4H), 4.01-4.04 (m, 4H), 4.36-4.39 (m, 4H), 6.85 (s, 2H), 8.09 (s, 2H). ^{13}C -NMR (CDCl_3 , 50.3 MHz): δ 26.44 (q), 61.55 (t), 67.81 (t), 69.34 (t), 70.20 (t), 70.52 (t), 70.57 (t), 70.93 (t), 72.40 (t), 103.39 (d), 117.97 (d), 119.31 (s), 145.83 (s), 160.08 (s), 161.34 (s). **16** ^1H -NMR (CDCl_3 , 300 MHz): δ 2.49 (s, 3H), 2.65 (s, 3H), 3.59-3.82 (m, 12H), 3.98-4.01 (m, 2H), 4.29-4.32 (m, 2H), 6.28 (s, 1H), 6.69 (s, 1H), 7.80 (d, 1H, $J = 9.0$ Hz), 8.12 (d, 1H, $J = 9.0$ Hz). ^{13}C -NMR (CDCl_3 , 50.3 MHz): δ 20.26 (q), 25.44 (q), 61.55 (t), 68.09 (t), 69.19 (t), 70.22 (t),

70.51 (t), 70.58 (t), 70.95 (t), 72.45 (t), 103.73 (d), 111.99 (d), 115.74 (d), 119.79 (s), 120.64 (d), 123.43 (s), 135.86 (s), 138.67 (s), 147.17 (s), 159.31 (s), 161.70 (s), 178.53 (s). HRMS: calcd. for $C_{22}H_{28}N_2O_6$: 416.195; found 416.196.

2-{2-[2-(2-{[2,9-dimethyl-7-(2-{2-[2-(2-{[(4-methylphenyl)-sulfonyl]-oxy}-ethoxy)-ethoxy]-ethoxy}-ethoxy)-1,10-phenanthroline-4-yl]-oxy}-ethoxy)-ethoxy]-ethoxy}-ethyl 4-methylbenzenesulfonate (17)

1.20 g (2.02 mmol) diol **15** was dissolved in 10 ml of THF and 40 ml of CH_2Cl_2 . To this stirred mixture 25 ml of 30% aqueous NaOH was added and the resulting biphasic system was cooled to 0 °C. A solution of 1.16 g (6.08 mmol) 4-methylbenzenesulfonyl chloride in 12 ml of THF was added dropwise keeping the temperature of the reaction mixture at 0 °C (circa 30 minutes). The mixture was stirred for an additional 30 minutes at 0 °C and was then allowed to reach room temperature. Stirring was continued overnight. The organic layer was separated and the water layer was extracted three times with 30 ml portions of CH_2Cl_2 . The combined organic layers were washed once with 50 ml brine. After drying on Na_2SO_4 the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography (silica; CH_2Cl_2 /EtOAc/ Et_3N 40:55:5) and a clear yellow oil was obtained (0.55 g, 0.61 mmol, 30%). 1H -NMR ($CDCl_3$, 300 MHz): δ 2.40 (s, 6H), 2.87 (s, 6H), 3.56-3.69 (m, 16H), 3.78-3.81 (m, 4H), 4.01-4.05 (m, 4H), 4.12-4.15 (m, 4H), 4.36-4.39 (m, 4H), 6.86 (s, 2H), 7.30 (d, 4H, $J = 8.2$ Hz), 7.77 (d, 4H, $J = 8.2$ Hz), 8.08 (s, 2H). ^{13}C -NMR ($CDCl_3$, 50.3 MHz): δ 21.56 (q), 26.51 (q), 67.89 (t), 68.60 (t), 69.18 (t), 69.38 (t), 70.51 (t), 70.68 (t), 70.95 (t), 103.43 (d), 118.00 (d), 119.35 (s), 127.88 (d), 129.76 (d), 132.86 (s), 144.75 (s), 145.87 (s), 160.15 (s), 161.40 (s).

{2-[2-(2-{2-[7-(2-{2-[2-(2-diethylamino-ethoxy)-ethoxy]-ethoxy}-ethoxy)-2,9-di-methyl-[1,10]phenanthroline-4-yloxy]-ethoxy}-ethoxy)-ethoxy]-ethyl}-diethyl-amine (18)

0.40 g (0.44 mmol) ditosylate **17** was added to a mixture of 0.92 g (6.7 mmol) potassium carbonate and 0.33 g (4.5 mmol) diethylamine in 10 ml of toluene. The reaction mixture was refluxed for 4 days and was then allowed to cool to room temperature. The suspension was filtered with suction on a glass filter P4 and the residue was washed three times with 10 ml of CH_2Cl_2 . The filtrate and the washings were combined and the solvents were evaporated *in vacuo*. The crude product was purified by column chromatography (silica; CH_3CN /MeOH/ Et_3N 18:1:1) yielding **18** as a pale brown, clear oil (192 mg, 0.273 mmol, 62%). 1H -NMR ($CDCl_3$, 300 MHz): δ 0.99 (t, 12H, $J = 7.0$ Hz), 2.54 (q, 8H, $J = 7.0$ Hz), 2.63 (t, 4H), 2.84 (s, 6H), 3.52-3.70 (m, 16H), 3.77-3.80 (m, 4H), 4.01 (t, $J = 4.8$ Hz, 4H), 4.35 (t, $J = 4.8$ Hz, 4H), 6.83 (s, 2H), 8.07 (s, 2H). ^{13}C -NMR ($CDCl_3$, 75.4 MHz): δ 11.44 (q), 26.46 (q), 47.47 (t), 52.13 (t), 67.84 (t), 69.36 (t), 69.51 (t), 70.32 (t), 70.48 (t), 70.61 (t), 70.96 (t), 103.36 (d), 117.99 (d), 119.35 (s), 145.91 (s), 160.07 (s), 161.38 (s). A correct *r* HRMS could not be obtained, although EI-MS gave *m/e* 703 (M+H).

7,22,25,40-tetramethyl-10,13,16,19,28,31,34,37-octaoxa-6,22,25,41-tetraazatetra-cyclo[36.4.0.0^{4,9}.0^{5,42}]dotetraconta-1(42),2,4,6,8,38,40-heptaene (19)

46 mg (0.52 mmol) *N,N'*-dimethylethylenediamine was added to a suspension of 0.52 g (1.6 mmol) cesium carbonate in 450 ml of toluene. 0.48 g (0.53 mmol) of ditosylate **17** in 10 ml toluene was added and the mixture was refluxed for 3 days. The mixture was allowed to cool to r.t. The suspension was filtered with suction on a glass filter P3 and the residue was washed three times with 20 ml of CH₂Cl₂. The filtrate and the washings were combined and the solvents were evaporated *in vacuo*. The crude oil was purified by preparative HPLC separation (silica; CH₃CN/MeOH/Et₃N 8:1:1; 0.3 ml/min) or by two successive flash column chromatographic separations (silica; CH₃CN/MeOH/Et₃N 18:1:1), yielding **19** in variable yield (5-26%). ¹H-NMR (CDCl₃, 300 MHz): δ 2.33 (s, 6H), 2.65 (s, 4H), 2.69 (t, 4H), 2.86 (s, 6H), 3.58-3.59 (m, 8H), 3.65-3.73 (m, 8H), 3.81-3.85 (m, 4H), 4.03 (dd, 4H), 4.36 (dd, 4H), 6.83 (s, 2H), 8.12 (s, 2H). ¹³C-NMR (CDCl₃, 50.3 MHz): δ 26.52 (q), 42.70 (q), 54.48 (t), 56.70 (t), 68.26 (t), 68.64 (t), 69.45 (t), 70.44 (t), 70.66 (t), 71.25 (t), 103.35 (d), 118.13 (d), 119.41 (s), 144.30 (s), 160.18 (s), 161.40 (s). HRMS: calcd. 644.379; no proper HRMS could be obtained, but ES-MS gave molecular ions at *m/e* 645 [M+H]⁺ and 323.5 [M+2H]²⁺.

Zinc complex of 3c

The diol **3c** (30 mg, 59 μmol) was suspended in 1 mL of CD₃CN and zinc perchlorate heptahydrate (22 mg, 59 μmol) was added. The solution became clear. The ¹H NMR spectrum showed quantitative conversion to the complex. The solvent was evaporated and the solid was crystallized from chloroform/acetone (1:1) with isothermal distillation of hexane into the solution affording zinc-**3c** as colorless crystals (37 mg, 47 μmol, 80%): ¹H NMR (300 MHz, CD₃CN/CDCl₃): δ 0.37 (s, 6H), 0.28 (s, 6H), 0.78 (s, 6H), 0.93 (m, 2H), 1.28 (m, 6H), 1.54 (m, 4H), 1.94 (m, 2H), 2.2 (br, H₂O), 3.30 (d, *J* = 16.48 Hz, 2H), 3.43 (d, *J* = 16.48 Hz, 2H), 5.40 (s, 2OH), 7.79 (d, *J* = 8.43 Hz, 2H), 7.89 (s, 2H), 8.50 (d, *J* = 8.43 Hz, 2H). ¹³C NMR: δ 9.92 (q), 19.31 (q), 20.09 (q), 24.96 (t), 30.20 (t), 43.42 (t), 43.76 (d), 45.61 (s), 48.72 (t), 52.66 (s), 88.14 (s), 125.73 (d), 126.91 (s), 127.19 (d), 133.05 (s), 140.88 (d), 160.01 (s); HRMS calcd 774.166; no proper HRMS could be obtained. Anal. Calcd for C₃₄H₄₄N₂O₁₀ZnCl₂: C, 52.56; H, 5.71; N, 3.61; Zn, 8.41. Found C, 52.46; H, 5.64; N, 3.63; Zn, 8.54.

Zinc complex of 7a

To a suspension of the ligand **7a** (48 mg, 88 μmol) in 1 mL of CD₃CN + 0.1 mL CDCl₃ was added zinc perchlorate heptahydrate (33 mg, 90 μmol). The ligand slowly dissolved within 5 min. and the reaction was analyzed by means of ¹H NMR, which indicated quantitative formation of the complex **20**. The solvent was removed under reduced pressure and the mixture was recrystallized from ethyl acetate/acetonitrile (1:1) by slow distillation of hexane into the solution (67 mg, 83 μmol, 95%): ¹H NMR (300 MHz, CD₃CN/CDCl₃): δ 2.2 (br, H₂O), 3.93 (s, 4H), 7.11 (m, 20H), 7.24 (d, *J* = 8.06 Hz, 2H), 7.48 (br, 2OH), 7.76 (dd, *J* = 8.06 Hz, *J* = 8.06

Hz, 2H), 7.87 (d, $J = 8.06$ Hz, 2H). ^{13}C NMR: δ 45.03 (t), 82.87 (s), 119.94 (d), 125.56 (d), 127.55 (d), 127.66 (d), 128.55 (d), 140.95 (s), 142.00 (d), 146.76 (s), 157.50 (s).

Copper complex of **7a**

The free ligand **7a** (50 mg, 91 μmol) was suspended in 3 mL of a mixture of acetonitrile and chloroform (2:1). $\text{Cu}(\text{acac})_2$ (26 mg, 99 μmol) was added and stirring continued overnight. The solvents were removed and the product recrystallized from ethyl acetate to afford the di copper complex **21** (35 mg, 36 μmol , 40%): ^1H NMR (300 MHz, $\text{CD}_3\text{CN}/\text{CDCl}_3$): δ -7.5, -1.3, 1.2, 2.0, 4.1, 6.6, 9.5, 10.5, 34.7, 61.2.

Complexation of **18 with $\text{CuPF}_6 \cdot 4\text{CH}_3\text{CN}$ (1:1 complex)** A colorless solution of 6.7 mg (18 μmol) $\text{Cu}(\text{PF}_6) \cdot 4\text{CH}_3\text{CN}$ in 1 mL of acetonitrile was added to solution of 12.6 mg (18 μmol) ligand **18** in 1.26 mL of acetonitrile via a canula. Immediately upon addition the solution turned bright orange. Two samples were taken: one was kept under N_2 , the other was exposed to air. The samples gave comparable mass spectra. ES-MS of a sample showed a lot of signals, among them: m/z 383 $[\text{Cu}^I + \text{ligand} + \text{H}]^{2+}$, 703.5 $[\text{ligand} + \text{H}]^+$, 765.6 $[\text{Cu}^I + \text{ligand}]^+$ and 1467.8 $[\text{Cu}^I + 2 \text{ ligands}]^+$. The solvent of the rest of the reaction mixture was evaporated *in vacuo* yielding a orange oil. ^1H -NMR (300 MHz, CDCl_3): δ 1.05 (br, 12H), 2.01 (s, CH_3CN), 2.38 (s, 6H), 2.67 (br, 12H), 3.63-3.81 (m, 20H), 4.07 (br, 4H), 4.48 (br, 4H), 7.10 (s, 2H), 8.24 (s, 2H).

Acknowledgements

We are grateful to Mr. J. Buter for initial experiments with the phenanthrolines.

References

1. a) Graham, B. in *Six-Membered Heterocyclic Nitrogen Compounds with Three Condensed Rings*, Wiley-Interscience, New York, **1958**, pp 386-456. b) Barigelletti, F.; Ventura, B.; Collin, J-P.; Kayhanian, R.; Gavina, P.; Sauvage, J-P. *Eur. J. Inorg. Chem.* **2000**, 113. c) Lüth, M.S.; Kapinos, L.E.; Song, B.; Lippert, B.; Sigel, H. *J. Chem. Soc., Dalton Trans.* **1999**, 357. d) Hurley, D.J.; Roppe, J.R.; Tor, Y. *Chem. Commun.* **1999**, 993. e) Blake, A.J.; Hill, S.J.; Hubberstey, P.; Li, W-S. *J. Chem. Soc., Dalton Trans.* **1998**, 909.
2. Weijnen, J.G.J.; Koudijs, A.; Engbersen, J. F.J. *J. Org. Chem.* **1992**, 57, 7258.
3. Siegman, D.S. *Biochemistry* **1990**, 29, 9097.
4. Peña-Cabrera, E.; Norrby, P-O.; Sjögren, M.; Vitagliano, A.; De Felice, V.; Oslob, J.; Ishii, S.; O'Neill, D.; Akermark, B.; Helquist, P. *J. Am. Chem. Soc.* **1996**, 118, 4299.
5. Gladiali, S.; Chelucci, G.; Soccolini, F. *J. Organomet. Chem.* **1989**, 370, 285.

6. Gladiali, S.; Pinna, L.; Delogu, G.; De martin, S; Zassinovich, G.; Mestroni, G. *Tetrahedron: Asymmetry* **1990**, *1*, 635.
7. a) Collins, J.E.; Lamba, J.J.S.; Love, J.C.; McAlvin, J.E.; Ng, C.; Peters, B.P.; Wu, X.; Fraser, C.L. *Inorg. Chem.* **1999**, *38*, 2020. b) Heseck, D.; Inoue, Y.; Everitt, S.R.L.; Ishida, H.; Kunieda, M.; Drew, M.G.B. *Inorg. Chem.* **2000**, *39*, 308. c) Wu, H-P.; Janiak, C.; Rheinwald, G.; Lang, H. *J. Chem. Soc., Dalton Trans.* **1999**, 183. d) Homanen, P.; Haukka, M.; Aklgrén, M.; Pakkanen, T.A.; Baxter, P.N.W.; Benfield, R.E. Conner, J.A. *J. Organomet. Chem.* **1998**, *552*, 205. e) Tzeng, B-C.; Fu, W-F.; Che, C-M.; Chao, H-Y.; Cheung, K-K.; Peng, S-M. *J. Chem. Soc., Dalton Trans.* **1999**, 1017. f) Hlec, D-H.; Murthy, N.N.; Karlin, K.D. *Inorg. Chem.* **1997**, *36*, 5785. g) Blake, A.J.; Gould, R.O.; Rawson, J.M.; Winpenny, R.E.P. *J. Chem. Soc., Dalton Trans.* **1994**, 2005. h) Wang, Z.; Reibenspies, J.; Motekaitis, R.; Martell, A.E. *J. Chem. Soc., Dalton Trans.* **1995**, 1511. i) Shu, M-H.; Duan, C-Y.; Sun, W-Y.; Fu, Y-J.; Zhang, D-H.; Bai, Z-H.; Tang, W-X. *J. Chem. Soc., Dalton Trans.* **1999**, 2317.
8. Bolm, C.; Schlingloff, G.; Harms, K. *Chem. Ber.* **1992**, *125*, 1191.
9. Bolm, C.; Zehnder, M.; Bur, D. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 205.
10. Nishiyama, H.; Yamaguchi, S.; Park, S.-B.; Itoh, K. *Tetrahedron: Asymmetry* **1993**, *4*, 143.
11. Kwong, H-L.; Lau, K-M.; Lee, W-S.; Wong, W-T. *New J. Chem.* **1999**, *23*, 629.
12. a) Ito, K.; Tabuchi, S.; Katsuki, T. *Synlett* **1992**, 575. b) Kwong, H-L.; Lee, W-S.; Ng, H-F.; Chiu, W-H.; Wong, W-T. *J. Chem. Soc., Dalton Trans.* **1998**, 1043. c) Rios, R.; Liang, J.; Lo, M.M.-C.; Fu, G.C. *Chem. Commun.* **2000**, 377.
13. Chelucci, G.; Pinna, G.A.; Saba, R. *Tetrahedron Assym.* **1998**, *9*, 531.
14. Summers, L.A. The Pyridinium Herbicides, Academic Press, London, **1980**
15. a) Leuning, U.; Mueller, M.; Gerbert, M.; Peters, Karl, Schnering, H.G. von; Keller, M. *Chem. Ber.* **1994**, *127*, 2297. b) Krakowiak, K.E.; Bradshaw, J.S.; Jiang, W.; Dalley, N.K.; Wu, G.; Izatt, R.M. *J. Org. Chem.* **1991**, *56*, 2675. c) Newkome, G.R.; Pappalardo, S.; Gupta, V.K.; Fronczek, F.R. *J. Org. Chem.* **1983**, *48*, 4848. d) Buhleier, E.; Wehner, W.; Voegtler, F. *Chem. Ber.* **1978**, *111*, 200. e) Smittel, M.; Ammon, H. *Chem. Commun.* **1995**, 687. f) Blake, A.J.; Casabo, J.; Devillanova, F.A., Escriche, L.; Garau, A.; Isaia, F.; Lippolis, V.; Kivekas, R.; Muns, V.; Schroder, M.; Sillanpaa, R.; Verani, G. *J. Chem. Soc., Dalton Trans.* **1999**, 1085. g) Blake, A.J.; Demartin, F.; Devillanova, F.A., Garau, A.; Isaia, F.; Lippolis, V.; Schroder, M.; Verani, G. *J. Chem. Soc., Dalton Trans.* **1996**, 3705. h) Himela, Y.; Hiratani, K.; Kasuga, K.; Hirose, T. *Chem. Lett.* **1993**, 1475.
16. a) Dietrich-Buchecker, C.O.; Hemmert, C.; Khemiss, A.-K.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1990**, *112*, 8002. b) Suk, J.; Lee, S.H. *J. Org. Chem.* **1998**, *63*, 1519.
17. a) Garcia, A.M.; Romero-Salguero, F.J.; Bassani, D.M.; Lehn, J.-M.; Baum, G.; Fenske, D. *Chem. Eur. J.* **1999**, *5*, 1803. b) Blake, A.J.; Hill, S.J.; Hubberstey, P.; Li, W-S. *J. Chem. Soc., Dalton Trans.* **1997**, 913. c) Baxter, P.N.W.; Lehn, J-M.; Kneisel, B.O.; Fenske, D. *Chem. Commun.* **1997**, 2231. d) Baxter, P.N.W. *J. Org. Chem.* **2000**, *65*, 1257. e) Tong, M-L.; Lee, H.K.; Chen, X-M.; Huang, R-B.; Mak, T.C.W. *J. Chem. Soc., Dalton Trans.* **1999**,

3657. f) Wärnmark, K.; Baxter, P.N.W.; Lehn, J-M. *Chem. Commun.* **1998**, 993. g) Lehn, J-M. *Supramolecular Chemistry*, VCH Weinheim, **1995**, p 143-160.
18. a) Koning, B.; Meetsma, A.; Kellogg, R.M. *J. Org. Chem.* **1998**, 63, 5533. b) Koning, B.; Buter, J.; Hulst, R.; Stroetinga, R.; Kellogg, R. M., *Eur. J. Org. Chem.* **2000**, 2735. c) Koning, B., Hulst, R., Bouter, A., Buter, J., Meetsma, A., Kellogg, R.M. *Chem. Commun.* **1997**, 1065
19. Imamoto, T.; Sugiura, Y.; Takiyama, N., *Tetrahedron Lett.* **1984**, 25, 4233-4236.
20. a) Schmittel, M; Ammon, H. *Synlett* **1997**, 1096-1098. b) Schmittel, M; Ammon, H *Eur.J.Org.Chem.* **1998**, 785-792. c) Schmittel, M.; Ammon, H.; Wöhrle, C. *Chem.Ber.* **1995**, 128, 845-850. d) Bell, T. W.; Hu, L.-Y.; Patel, S. V. *J.Org.Chem.* **1987**, 52, 3847-3850
21. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Deposition numbers are 221384 and 221385. Copies of the data can be obtained free of charge on application to the Director. CCDC, 12 union road, Cambridge CB2 1EZ, UK (Fax. Int code +(1223)336-033, E-MAIL: teched@chemcrys.cam.ac.uk).
22. Compared to hydroxylate bridged di-copper complexes found in the Cambridge Crystallographic Database.
23. Jeener, J.; Meier, B.H.; Bachmann, P.; Ernst, R.R., *J. Chem. Phys.* **1979**, 71, 4546. b) Neuhaus, D.; Williamson, M., in *The Nuclear Overhauser Effect in Structural and Conformational Analysis*, VCH Publishers: Cambridge, **1989**.
24. Bax, A.; Freeman, R. *J. Magn. Reson.* **1981**, 44, 542.
25. Dried according to the literature procedure described by Martin, S.F. *Organic Synthesis* Vol. 76, **1998**, p.228.
26. The commercial available material was recrystallized from toluene to afford the anhydrous material.
27. Rode, T.; Breitmaier, E. *Synthesis* **1987**, 6, 574.